INFRARED STUDIES OF SOME ORGANIC COMPOUNDS

BY

ROBERT McLAUGHLIN WHITNEY
B.A., Augustana College,
Sioux Falls, South Dakota, 1936

AN ABSTRACT OF A THESIS

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INTRODUCTION

In recent years, certain stable enols which do not appear to be stabilized by chelation have been synthesized by organic chemists, particularly Dr. R. C. Fuson and his co-workers.[1-5] These compounds are substituted vinyl alcohols in which the substituents consist of one or more sterically hindering groups of the type: mesityl, isoduryl, triisopropylphenyl, etc.

As a result of extensive experimentation, the following generalizations have been made:

1) Keto enols bearing at least two sterically hindering groups and an additional hydrocarbon residue will possess unusual stability.

2) Aldehyde enols possessing at least one hindering group and a hydrocarbon residue will possess unusual stability.

3) Under other conditions of substitution, ketones or aldehydes only are obtained from reactions expected to yield enols.

In certain cases, it has been found possible to ketonize these enols by vigorous treatment and, when once formed, these ketones are quite stable. However, since cis and trans isomers of these enols are possible and since the ketones formed in which there are no hindering groups in the alpha positions form enol acetates, some doubt as to the structure of these compounds exists when based on chemical reactions only.

Infrared spectroscopy, however, serves as a valuable tool in verifying the structure of these compounds and, since it is also possible to determine structural phenomena involving interactions between atoms of a smaller order of magnitude than chemical bonds, it was thought that some light might be thrown on the reason for the unusual stability of these compounds.

EXPERIMENTAL RESULTS

Two spectrometers were used in this study. In the preliminary work, a rock salt prism spectrometer was used, and, for higher resolution, a grating spectrometer was employed. These instruments have been described in previous publications.[6-7]

All compounds investigated were prepared by Dr. R. C. Fuson and his co-workers and were studied in carbon tetrachloride solution at concentrations and cell lengths indicated in the tables.

investigators,[16] the three shorter wave length peaks can be attributed to aromatic C-H valence vibrations and the three highest to the C-H valence vibrations in a methyl group. Some of the aromatic C-H maxima are not observed in some of the compounds studied, probably due to masking by stronger neighboring obsorption. The lower of the three aliphatic C-H maxima appears to be a doublet but further experimentation with higher resolutions and higher intensities are necessary before this can be established. There also appears to be another peak at 3.322-3.364 μ.

6 μ Absorption Bands

The spectral maxima observed in the 6 μ region can be divided into those attributed to the carbonyl valence vibrations and those assigned to the carbon-carbon double bond vibration. The absorption observed at from 5.876-5.903 μ in the ketones and at 5.76 μ in ethyl dimesityl acetate corresponds to that observed by Barnes, Liddel, and Williams[17] in similar carbonyl compounds and can be attributed to the carbonyl valence vibration.

The maxima observed above 6 μ in all the compounds containing an ethylenic double bond except pentene-2 corresponds to that observed by other investigators[17] in compounds containing an ethylenic double bond and sufficient asymmetry to possess a permanent dipole moment. Therefore it can be attributed to the valence vibration of the ethylenic double bond.

The absence of carbonyl absorption in the spectra of the substituted vinyl alcohols denies the possibility of a keto-enol equilibrium in othese compounds in carbon tetrachloride solutions.

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VITA

Robert McLaughlin Whitney was born in St. Paul, Minnesota, on September 28, 1911. He was tutored privately for the first four years of elementary school in Fargo, North Dakota. In 1920, he entered the public schools of Sious Falls, South Dakota. From 1925-1929, he attended Washington High School in Sious Falls. After three years in industry, he returned to school at Augustana College, Sioux Falls, South Dakota, receiving his Bachelor of Arts degree from there in August, 1936. During the year 1936-37 he was a part time Instructor in Mathematics at Augustana College. The next year was spent as Head of the Science Department at the Harvey High School, Harvey, North Dakota. During the summer of 1938, he attended the Southern Illinois Normal University at Carbondale, Illinois. That fall he was appointed Head of the Science Department at the Cairo High School, Cairo, Illinois, where he remained until the fall of 1940. In the summer of 1939 he enrolled in the Graduate School of the University of Illinois. During the second year at Cairo High School, he was elected Secretary of the Southern Illinois Chemistry Teachers Association. On August 15, 1940, he secured a position as Assistant Chemist for the Illinois State Water Survey, which enabled him to pursue his graduate study. In the fall of 1942, he was made half time Instructor in Chemistry at the University of Illinois and then, in the spring, full time Instructor in Chemistry there. During the summer of 1943, he served as Special Research Assistant for the National Defense Research Committee. At present he is Instructor in Chemistry at the University of Illinois. He is an associate member of Sigma Xi. His publications consist of N. D. R. C. Reports.

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